

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:
A01N 43/80 // (A01N 43/80, 43:10, 37:22)
A1 (11) International Publication Number: WO 97/34485
(43) International Publication Date: 25 September 1997 (25.09.97)

(21) International Application Number:

PCT/EP97/01055

(22) International Filing Date:

3 March 1997 (03.03.97)

(30) Priority Data:

692/96

15 March 1996 (15.03.96)

CH

(71) Applicant (for all designated States except US): NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): RÜEGG, Willy [CH/CH]; Felmetweg 6, CH-5073 Gipf-Oberfrick (CH).

(74) Common Representative: NOVARTIS AG; Patent- und Markenabteilung, Lichtstrasse 35, CH-4002 Basel (CH). (81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

#### **Published**

With international search report.

(54) Title: HERBICIDAL SYNERGISTIC COMPOSITION AND METHOD OF WEED CONTROL

#### (57) Abstract

The invention relates to a herbicidal composition, comprising, besides conventional inert formulation assistants, a compound of formula (I) [S], wherein  $R_1$  is the  $(A_1)$  or  $(A_2)$  group and a synergistically effective amount of the active ingredient of formula (II).

$$C_2H_6$$
 (A<sub>1</sub>)  $C_3H_6$  (A<sub>2</sub>)

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia	
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia	
· AT	Austria	FR	France	LU	Luxembourg	SN	Senegal	
AU	Australia	GA	Gabon	LV	Latvia	<b>8Z</b>	Swaziland	
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad	
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo	
BB	Barbados	GH	Ghana	MG	Madagascar	Tj	Tajikistan	
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan	
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey	
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago	
BJ	Benin	IE	ireland	MN	Mongolia	UA	Ukraine	
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda	
BY	Belanus	IS	Iceland	MW	Malawi	US	United States of America	
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan	
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam	
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia	
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe	
a	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand			
CM	Cameroon		Republic of Korea	PL	Poland			
CN	China	KR	Republic of Korea	PT	Portugal			
CU	Cuba	KZ	Kazakstan	RO	Romania			
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation			
DE	Germany	u	Liochtenstein	SD	Sudan			
DK	Denmark	LK	Sri Lanka	SE	Sweden			
KE	Estonia	LR	Liberia	SG	Singapore			

## Herbicidal synergistic composition and method of weed control

The present invention relates to a novel herbicidal synergistic composition that comprises a combination of herbicides suitable for selectively controlling weeds in crops of cultivated plants, typically in crops of cereals, maize, rice, rape, sugar beet, sugar cane, plantations, cotton and soybeans.

The invention further relates to a process for controlling weeds in crops of cultivated plants and to the use of said novel composition therefor.

wherein R<sub>1</sub> is the

$$H_3C$$
 $C_2H_5$ 
 $C_2H_5$ 
 $C_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

have herbicidal activity, as is disclosed, inter alia, in US-A-5 002 606 and US-A-5 457 085.

The following compound of formula II

is also known as herbicide, inter alia from BRIGHTON CROP PROTECTION CONFERENCE - Weeds - 1995, Proceedings Volume 1, pages 35 - 42. Synergistic mixtures of compounds of formula II with the racemates of formula I are disclosed in WO 96/03877.

Surprisingly, it has now been found that a variable amount of a combination of two active ingredients, i.e. of an active ingredient of formula I with an active ingredient of formula II exerts a synergistic effect that is able to control the majority of weeds preferably occurring in crops of cultivated plants preemergence as well as postemergence, without substantial injury to the cultivated plants.

Accordingly, this invention proposes a novel synergistic composition for selectively controlling weeds, which comprises, in addition to conventional inert formulation assistants, as active ingredient on the one hand a compound of formula I

wherein R<sub>1</sub> is the

$$H_3C$$
 $C_2H_5$ 
 $(A_1)$  or
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

and, on the other hand, a synergistically effective amount of the active ingredient of formula II

in admixture with each other.

WO 97/34485

The compounds of formula I are the optical isomers aRS,1'S(-)-N-(1'-methyl-2'-methoxy-ethyl)-N-chloroacetyl-2-ethyl-6-methylaniline and (1S,aRS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide.

It is highly surprising that the combination of an active ingredient of formula I with an active ingredient of formula II has a greater additive action against the weeds to be controlled than to be expected in principle and thus enhances the activity range of both active ingredients in particular in two respects:

On the one hand, the rates of application of the single compounds I and II are reduced while the effectiveness of said compounds is retained. On the other hand, the novel combination also achieves a high degree of weed control where the single compounds have become no longer agriculturally effective at low rates of application. The consequence is a substantial broadening of the activity spectrum against weeds and an additional increase in the selectivity for the cultivated plants that is necessary and desirable in the event of unintentional overapplication of herbicide. Furthermore, the novel composition permits more flexibility in subsequent crops while retaining the excellent control of weeds in cultivated plants.

The novel herbicidal compostions can be used against a great number of agriculturally important weeds, including Stellaria, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica.

The novel compositions are suitable for all standard methods of application used in agriculture, typically preemergence application, postemergence application and seed dressing.

The novel herbicidal combination is preferably suitable for weed control in crops of cultivated plants, typically cereals, rape, sugar beet, sugar cane, plantations, rice, maize and soybeans as well as for non-selective weed control. The novel combination is preferably used in maize and soybeans.

Crops will be understood as meaning also those crops that have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods.

The novel herbicidal combination contains the active ingredient of formula I and the active ingredient of formula II in any ratio, but usually with an excess of the one component over the other. Preferred ratios of the active ingredient of formula I and the component of formula II are in the range from 1:100 to 100:1, prefererably from 1:10 to 10:1.

Very particularly effective synergistic herbicidal compositions have been found to be combinations of the compound of formula I, wherein R<sub>1</sub> is the A<sub>1</sub> group, with the compound of formula II.

In addition to the compounds of formulae I and II, the novel compositions can contain a safener, in particular Benoxacor. Benoxacor is known, inter alia, from The Pesticide Manual, 9th ed., The British Crop Protection Council, page 61. Benoxacor is known as safener for protecting cultivated plants against the herbicidal action of the compounds of formula I, in particular against that compound of formula I, wherein R<sub>1</sub> is the A<sub>1</sub> group.

If the novel composition contains a safener, the weight ratio of herbicide of formula I (in particular that of compound of formula I, wherein R<sub>1</sub> is the A<sub>1</sub> group) to safener is preferably from 5:1 to 40:1, in particular from 20 to 1.

Different methods and techniques may suitably be used for applying safeners or compositions containing them for protecting cultivated plants from the harmful effects of herbicides of formula I, conveniently the following:

#### i) Seed dressing

WO 97/34485

- a) Dressing the seeds with a wettable powder formulation of the safener by shaking in a vessel until the safener is uniformly distributed on the surface of the seeds (dry treatment), using up to c. 1 to 500 g of the active ingredient of formula  $\Pi$  (4 g to 2 kg of wettable powder) per 100 kg of seeds.
- b) Dressing seeds with an emulsifiable concentrate of the safener by method a) (wet treatment).

c) Dressing by immersing the seeds in a mixture containing 100-1000 ppm of the safener for 1 to 72 hours, leaving them wet or subsequently drying them (seed soaking).

Seed dressing or treatment of the germinated seedlings are naturally the preferred methods of application, as the safener treatment is fully concentrated on the target crop. Usually 1 to 1000 g, preferably 5 to 250 g, of antidote is used per 100 kg of seeds. However, depending on the method employed, which also permits the use of other active ingredients or micronutrients, plus or minus deviations from the indicated limiting concentrations are possible (repeat dressing).

#### ii) Application as tank mixture

A liquid formulation of a mixture of antidote and herbicide (reciprocal ratio from 10:1 to 1:100) is used, the concentration of herbicide being from 0.05 to 4.0 kg/ha. Such tank mixtures are applied before or after sowing.

#### iii) Application in the furrow

The safener formulated as emulsifiable concentrate, wettable powder or granulate is applied to the open furrow in which the seeds have been sown. After covering the furrow, the herbicide is applied pre-emergence in conventional manner.

#### iv) Controlled release of safener

A solution of the safener is applied to mineral granulate substrates or polymerised granulates (urea/formaldehyde) and dried. A coating may additionally be applied (coated granulates) which permits controlled release of the safener over a specific period of time.

The rate of application can vary over a wide range and will depend on the nature of the soil, the type of application (pre- or postemergence, seed dressing, application to the seed furrow; no tillage application etc.), the cultivated plant, the weed to be controlled, the respective prevailing climatic conditions; and on other factors governered by the type of application and the target crop. The herbicidal combination can usually be applied in a rate of application of 0.05 to 4 kg, preferably of 0.5 to 4 kg/ha.

The combinations of the compound of formula I with the compound of formula II may be used in unmodified form, i.e. as obtained in the synthesis, but preferably they are processed in

conventional manner with the assistants customarily employed in formulation technology, typically solvents, solid carriers or surfactants, e.g. to emulsifiable concentrates, directly sprayable or dilutable solutions, wettable powders, soluble powders, dusts, granulates or microcapsules. As with the type of compositions, the methods of application such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the compositions containing the active ingredients of formulae I and II and optionally one or more than one formulation assistants, are prepared in per se known manner, e.g. by homogeneously mixing and/or grinding the active ingredient with said formulation assistants, typically solvents or solid carriers. Surface-active compounds (surfactants) may additionally be used for preparing the formulations.

Suitable solvents may typically be: aromatic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms such as mixtures of xylene or substituted naphthalenes; phthalates such as dibutyl phthalate or dioctyl phthalate; aliphatic hydrocarbons such as cyclohexane or paraffins; alcohols and glycols and their ethers and esters such as ethanol, ethylene glycol, 2-methoxyethanol or 2-ethoxyethanol; ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethylsulfoxide or N,N-dimethylformamide, as well as vegetable oils or epoxidised vegetable oils such as epoxidised coconut oil or soybean oil; or water.

The solid carriers typically used for dusts and dispersible powders are usually natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. To improve the physical properties it is also possible to add highly dispersed silicic acid or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, including pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are materials such as calcite or sand. In addition, innumerable pregranulated materials of inorganic or organic origin may be used, especially dolomite or pulverised plant residue.

Depending on the type of active ingredient of formula I to be formulated, suitable surfaceactive compounds are nonionic, cationic and/or anionic surfactants or mixtures of surfactants having good emulsifying, dispersing and wetting properties. Suitable anionic surfactants may be water-soluble soaps as well as water-soluble synthetic surface-active compounds.

Suitable soaps are the alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts of higher fatty acids (C<sub>10</sub>-C<sub>22</sub>), e.g. the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained, inter alia, from coconut oil or tallow oil. Further suitable soaps are also the fatty acid methyl taurin salts.

More often, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and they contain a C<sub>8</sub>-C<sub>22</sub>alkyl radical which also includes the alkyl moiety of acyl radicals, e.g. the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfate, or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain two sulfonic acid groups and one fatty acid radical containing 8 to 22 carbon atoms. Illustrative examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid, or of a condensate of naphthalenesulfonic acid and formaldehyde.

Corresponding phosphates, typically salts of the phosphoric acid ester of p-nonylphenol-(4-14)ethylene oxide, or phospholipids, are also suitable.

Nonionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols or of saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols.

Further suitable nonionic surfactants are the water-soluble polyadducts of poylethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which polyadduccts contain 20 to

250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Illustrative examples of nonionic surfactants are nonylphenol polyethoxylates, polyethoxylated castor oil, polyadducts of polypropylene and polyethylene oxide, tributylphenol polyethoxylate, polyethylene glycol and octylphenol polyethoxylate.

Fatty acid esters of polyoxyethylene sorbitan are also suitable nonionic surfactants, typically polyoxyethylene sorbitan trioleate.

Cationic surfactants are preferably quaternary ammonium salts carrying, as N-substituent, at least one C<sub>8</sub>-C<sub>22</sub> alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, for example stearyl trimethylammonium chloride or benzyl bis(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in the art of formulation are described, inter alia, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, München/Wien, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New. York, 1980-81.

The herbicidal formulations usually contain from 0.1 to 99 % by weight, preferably from 0.1 to 95 % by weight, of active ingredient mixture of the compound of formula I with the compound of formula II, from 1 to 99.9 % by weight of a solid or liquid formulation assistant, and from 0 to 25 % by weight, preferably from 0.1 to 25 % by weight, of a surfactant.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The compositions may also contain further ingredients such as stabilisers, vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rape seed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders, tackifiers, as well as fertilisers or other active ingredients.

Preferred formulations are those composed of: (% = percent by weight)

Emulsifiable concentrates:

compound mixture:

1 to 90 %, preferably 5 to 20 %

surfactant:

1 to 30 %, preferably 10 to 20 %

liquid carrier:

5 to 94 %, preferably 70 to 85 %

Dusts:

compound mixture:

0.1 to 10 %, preferably 0.1 to 5 %

solid carrier:

99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

compound mixture:

5 to 75 %, preferably 10 to 50 %

water:

94 to 24 %, preferably 88 to 30 %

surfactant:

1 to 40 %, preferably 2 to 30 %

Wettable powders:

compound mixture:

0.5 to 90 %, preferably 1 to 80 %

surfactant:

0.5 to 20 %, preferably 1 to 15 %

solid carrier:

5 to 95 %, preferably 15 to 90 %

Granulates:

compound mixture:

0.1 to 30 %, preferably 0.1 to 15 %

solid carrier:

99.5 to 70 %, preferably 97 to 85 %

**b**)

The invention is illustrated by the following non-limitative Examples.

Formulation Examples for mixtures of herbicides of formulae I and II (% = percent by weight)

F1. Emulsifiable concentrates a)

c)

6 %

sulfonate

compound mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
polyethoxylated castor oil	4 %	-	4 %	4 %
(36 mol EO)				
octylphenol polyethoxylate	-	4 %	-	2 %
(7-8 mol EO)				
cyclohexanone	-	•	10 %	20 %
mixture of aromatic				
hydrocarbons C <sub>9</sub> -C <sub>12</sub>	85 %	78 %	55 %	16 %
Emulsions of any desired concentrations water.	ration can be	e prepared by diluti	ng such concentra	tes with
F2. Solutions	a)	b)	c)	d)
compound mixture	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy-	0 /0			
propoxy)propane	•	20 %	20 %	-
polyethylene glycol MG 400	20 %	10 %	-	
N-methyl-2-pyrrolidone	_	<u>-</u>	30 %	
10 %				
mixture of aromatic				
hydrocarbons C <sub>9</sub> -C <sub>12</sub>	75 %	60 %	-	-
The solutions are suitable for use	as microdro	ops.		
F3. Wettable powders	a)	<b>b</b> )	c)	d)
compound mixture	5 %	25 %	50 %	80 %
sodium ligninsulfonate	4 %	-	3 %	-
sodium laurylsulfate	2 %	3 %	-	4 %
sodium diisobutylnaphthalene-				
				/ O/:

6 %

5 %

octylphenol polyethoxylate	-	1 %	2 %	-
(7-8 mol EO)				
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	•

The compound is thoroughly mixed with the adjuvants and this mixture is ground well in a suitable mill to give wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granulates	a)	b)	c)
compound mixture	0.1 %	5 %	15 %
highly dispersed silicic acid	0.9 %	2 %	2 %
inorganic carrier	99.0 %	93 %	83 %
(Æ 0.1 - 1 mm)			
e.g. CaCO <sub>3</sub> or SiO <sub>2</sub>			

The compound is dissolved in methylene chloride, the solution is sprayed on to the carrier, and the solvent is removed under vacuum.

F5. Coated granulates	a)	b)	c)
compound mixture	0.1 %	5 %	15 %
polyethylene glycol MG 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier	98.0 %	92 %	80 %
(Æ 0.1 - 1 mm)			
e.g. CaCO <sub>3</sub> or SiO <sub>2</sub>			

The finely ground compound is uniformly applied in a mixer to the carrier moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F6. Extruder granulates	a)	b)	c)	d)
-------------------------	----	----	----	----

WO 97/34485 PCT/EP97/01055

- 12 -

compound mixture	0.1 %	3 %	5 %	15 %
sodium ligninsulfonate	1.5 %	2 %	3 %	4 %
carboxymethyl cellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The compound is mixed with the adjuvants and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	ь)	c)
compound mixture	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready for use dusts are obtained by mixing the compound with the carriers on a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
compound mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyethoxylate	-	1 %	2 %	-
(15 mol EO)				
sodium ligninsulfonate	3 %	3 %	4 %	5 %
carboxymethyl cellulose	1 %	1 %	1 %	1 %
37% aqueous formaldehyde	0.2 %	0.2 %	0.2 %	0.2 %
solution				
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8
%				
water	87 %	79 %	62 %	38 %

The finely ground compound is intimately mixed with the adjuvants to give a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

WO 97/34485 PCT/EP97/01055

- 13 -

It is often more expedient to formulate the active ingredient of formula I and the component of formula II individually and only to combine them shortly before application in the applicator in the desired mixture ratio as tank mixture in water.

# Biological Examples:

Example H1: The following test compares the action of a composition of this invention, comprising as active ingredients the enantiomer aRS,1'S(-)-N-(1'-methyl-2'-methoxyethyl)-N-chloroacetyl-2-ethyl-6-methylaniline of formula Ia

and the compound of formula II

DISCLOSURE, April 1995/271, No. 37242, comprising the racemic compound N-(1'-methyl-2'-methoxyethyl)-N-chloroacetyl-2-ethyl-6-methylaniline of formula A

and the cited compound of formula II.

#### Pre-emergence application in maize:

Monocot and dicot weeds and cultivated plants (maize P3737) are sown in plastic pots in standard soil. Immediately after sowing, the test substances are applied in aqueous suspension (500 l water/ha). The rates of application for the compound of formula Ia or its racemate are

WO 97/34485

1000, 500 and 250 g/ha, and the rate of application for the compound of formula II is 120 g/ha. The test plants are then raised in a greenhouse under optimum conditions. Evaluation is made after 4 weeks (% action, 100 % = plant withered, 0 % = no phytotoxic action). The results are shown in the following Table B1.

Table B1: Herbicidal action in crops of maize:

Plant	Novel composition			Composition of the prior art		
	1000 g/ha Ia + 120 g/ha II	500 g/ha Ia + 120 g/ha II	250 g/ha Ia + 120 g/ha II	1000 g/ha A + 120 g/ha II	500 g/ha A + 120 g/ha II	250 g/ha A + 120 g/ha II
Maize	10	5	0	20	10	5
abutilon	100	100	100	100	100	100
theophrasti						
amaranthus	100	100	100	100	100	100
retroflexus						
euphorbia	100	98	98	95	95	95
heterophylla						
panicum	100	100	100	100	100	100
miliaceum						
setaria faberi	100	100	100	100	100	100
sorghum	100	100	100	100	100	100
bicolor						
xanthium	95	95	90	90	90	90
canadense						

Table B1 shows that the composition of this invention has advantages with respect to the herbicidal action in the weeds Euphorbia heterophylla and Xanthium canadense. This is taken to be the result of the enhanced herbicidal activity of the enantiomer of formula Ia over the racemate of formula A. Surprisingly, however, it is found that despite this enhanced activity the damage that the novel composition causes on maize is reduced by 50 % as compared to the known composition. At a rate of application of 250 g/ha of formula Ia there is even no damage at all to be observed on the cultivated plants, whereas the composition of the prior art at this rate of application damages the cultivated plant already to 5 %. The enhanced protection of the maize by the novel composition is of extremely great agricultural importance

WO 97/34485 PCT/EP97/01055

- 16 -

and is completely unexpected given the content of the more active enantiomer compared to the known racemate. A valuable practical consequence thereof is that the unintentional overapplication of the novel composition in maize is substantially less critical than in the case of the racemic composition.

Comparable results are obtained for the mixture of the compound of formula I, wherein A is  $A_2$ , with the compound of formula II.

## What is claimed is:

1. A herbicidal synergistic composition, comprising, besides conventional inert formulation assistants, a compound of formula I

wherein R<sub>1</sub> is the

$$H_3C$$
 $C_2H_5$ 
 $C_2H_5$ 
 $C_3$ 
 $CH_3$ 
 $CH_3$ 

and a synergistically effective amount of the active ingredient of formula II

- 2. A herbicidal composition according to claim 1, comprising a compound of formula I, wherein  $R_1$  is the  $A_1$  group.
- 3. A herbicidal composition according to claim 1, wherein the weight ratio of the component of formula I to the component of formula II is from 1:100 to 100:1.
- 4. A method of controlling undesirable plant growth in crops of cultivated plants, which comprises treating the cultivated plant or the locus thereof with a herbicidally effective amount of a composition as claimed in claim 1.

- 5. A method according to claim 4, wherein the cultivated plants are cereals, rape, sugar beet, sugar cane, plantations, rice, maize or soybeans.
- 6. A method according to claim 4, which comprises treating the crops of cultivated plants with the claimed composition in rates of application corresponding to 0.05 to 4 kg of total amount of active ingredient per hectare.
- 7. A composition according to claim 1, comprising, in addition to the compounds of formulae I and II, benoxacor.
- 8. A method according to claim 4, which comprises treating the cultivated plant or the locus thereof at separate times with the compound of formula I and with the compound of formula II.
- 9. A method according to claim 4, which comprises treating the cultivated plant or the locus thereof at separate times with the compound of formula I together with benoxacor and with the compound of formula II.

ttional Application No PLT/EP 97/01055

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N43/80 //(A01N43/80,43:10,37:22) According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 6 A01N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Y WO 96 03877 A (RHONE POULENC AGRICULTURE) 1-9 15 February 1996 cited in the application see page 2, line 4 - line 11 see page 3, line 15 - line 29 see page 5, line 7 - line 9 see page 5, line 12 - line 14 see claim 14 Y EP 0 614 606 A (SANDOZ LTD ;SANDOZ AG 1,3-9 (DE); SANDOZ AG (AT)) 14 September 1994 see page 2, line 1 - line 3 see page 2, line 10 Y US 5 002 606 A (MOSER HANS ET AL) 26 1-9 March 1991 see column 4, line 9 - line 24 -/--Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance noznavni 'E' earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority daim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or other means s, such combination being obvious to a person skilled "P" document published prior to the international filing date but later than the priority date claimed in the art. "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 2 June 1997 16.06.1997 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Td. (+31-70) 340-2040, Tx. 31 651 epo nl, Lamers, W Fax: (+31-70) 340-3016

Form PCT/ISA/210 (second sheet) (July 1992)

1

Ir tional Application No PLT/EP 97/01055

		PC1/EP 9//01055
C.(Continua	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Υ	US 5 457 085 A (SECKINGER KARL ET AL) 10 October 1995 see column 2, line 6 - line 9	1,3-9
Y	RESEARCH DISCLOSURE, no. 372, 1 April 1995, page 271/272 XP000509081 "NEUE HERBIZIDE MITTEL" cited in the application see the whole document	7,9
Υ	EP 0 685 157 A (CIBA GEIGY AG) 6 December 1995 see page 4, line 17 - line 54 see page 11, line 45 - line 55	7,9
Υ	EP 0 616 770 A (CIBA GEIGY AG) 28 September 1994 see page 4, line 16 - line 43 see page 11, line 54 - page 12, line 9	7,9
A	CHEMICAL ABSTRACTS, vol. 97, no. 9, 30 August 1982 Columbus, Ohio, US; abstract no. 71671, H.MOSER ET AL.: "Effect of atropisomerism and chiral center on the biological activity of Metolachlor" XP002032068 see abstract & Z.NATURFORSCH., vol. 37B, no. 4, 1982, pages 451-462,	1-9

1

Information on patent family members

Ir stional Application No
PUT/EP 97/01055

		1	PC1/EP 9//01055
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9603877 A	15-02-96	AU 3162595 BG 100530	A 29-11-96
		CA 2171853 CN 1131379	
		CZ 9601235	* -
		EP 0721298	
		PL 313790 SK 55396	
		ZA 9506143	
EP 0614606 A	14-09-94	AU 672264	
		AU 5515794 BE 1007930	
		BR 9400602	
		BR 9402537	
		CA 2115863	A 19-08-94
		CA 2126602	
		CN 1091240 CZ 9400345	
		DE 4421342	
		FR 2706735	
		FR 2727291 GB 2279872	
		GB 2279872 HR 940114	· • · · · · · · · · · · · · · · · · · ·
		HU 66739	
		HU 67562	
		JP 7017807 PL 302265	
		US 5491124	
		US 5545607	' A 13-08-96
		ZA 9404565	
		SK 18894 ZA 9401139	
US 5002606 A	26-03-91	BR 8206030	
		CA 1187901	
		EP 0077755 JP 1650377	
		JP 3009899	
		JP 58079964	13-05-83
	·		

Information on patent family members

fr tional Application No PUT/EP 97/01055

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5457085 A	10-10-95	NONE	
EP 0685157 A	06-12-95	AU 2045195 A	14-12-95
		BG 99687 A	29-12-95
		BR 9502648 A	09-04-96
		CA 2150781 A	04-12-95
		CN 1113410 A	20-12-95
		CZ 9501420 A	13-12-95
		FI 952651 A	04-12-95
		JP 7330506 A	19-12-95
		LV 11247 B	20-10-96
		NO 952203 A	04-12-95
		NZ 272257 A	29-01-97
		PL 308822 A	11-12 <b>-</b> 95
		SK 73295 A	06-12-95
		ZA 9504553 A	04-12 <b>-</b> 95
		HU 71509 A	28-12-95
EP 0616770 A	28-09-94	US 5556828 A	17-09-96

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

# **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:
☐ BLACK BORDERS
☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
☐ FADED TEXT OR DRAWING
BLURRED OR ILLEGIBLE TEXT OR DRAWING
☐ SKEWED/SLANTED IMAGES
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
☐ GRAY SCALE DOCUMENTS
☐ LINES OR MARKS ON ORIGINAL DOCUMENT
REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
OTHER.

# IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.